

Two Dimensional Dynamic Modeling of Hydrodesulphurization Reactor

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Abstract- In this research a pseudo-homogeneous two-dimensional model was proposed to describe the dynamic behavior of a fixed-bed pilot-plant hydrodesulphurization reactor. The catalyst pellet used in this reactor was Co-Mo/Al₂O₃. At first, using the experimental data, a power law kinetic model was developed for hydrodesulphurization reaction. Then a pseudo-homogeneous two-dimensional dynamic model was proposed to describe the concentration profile in the reactor bed. The simulation obtained with the proposed dynamic model showed good agreement with experimental data and the sulfur concentration error in the reactor outlet was 3.8 percent compared to the experimental data. Two dimension modeling revealed that the radial variation of sulfur concentration is more in the reactor inlet than the outlet, but in general the concentration profile can be considered in one dimension. Unsteady reactor modeling showed that the transition time was higher in the reactor outlet and estimated to be 11667 seconds.

Keywords- Hydrotreating reactor, Dynamic Modeling, Two Dimension

I. INTRODUCTION

Hydrodesulphurization (HDS) is an important process in oil industry. The HDS process is essential to obtain fuels with improved quality and low polluting compounds and it is usually conducted in a fixed-bed catalytic reactor either in single gas-phase flow or two phases (gas and liquid) [1-3] and usually a trickle-flow regime may occur. In the trickle flow regime, the liquid reactant flows downward through the reactor in the form of thin laminar film droplets around the solid catalyst [4-6]. Modeling and simulation are commonly applied in the design, performance analysis, optimization, and scale-up of HDS reactors. More papers in modeling and simulation are in steady state but reliable three-phase reactor modeling and simulation should be based on dynamic heterogeneous models, which can be used not only for scale-up, start-up and operability studies, but also to obtain a meaningful continuity path to the steady state of the reactor, since dynamic models provide a realistic description of the transient states of three-phase reactors [7, 8]. The study of the dynamic behavior of the three phase reactor also helps designing the best control system in order to obtain a safe, efficient and profitable operation. Although the dynamic models are more complicated to formulate and to solve, they should be preferred over steady-state models because the numerical solution strategy of dynamic models is more robust than the solution of steady-state models [9-12].

Numerous papers have been published on steady state modeling of hydrotreating reactors. However, studies on dynamic modeling of such reactors are reported less in the open literature among which the two dimensional models are rarely reported. Julcour et. al.[13] investigated the dynamic of the three phase up-flow fixed bed reactor using a non-isothermal heterogeneous model. They compared a simplified

model with an extended one and concluded that the diffusion of hydrocarbons is not limiting agent so that the simplified model predicts accurately the reactor transient behavior. Hastaoglu and Jibril[12] modeled the transient gas-solid reactions in a fixed-bed reactor and applied to HDS reaction with the Langmuir-Hinshelwood mechanism. They validated the model through a comparison of experimental data from naphtha HDS pilot plant. Mederos et. al[14] investigated a dynamic heterogeneous one-dimensional model of trickle-bed hydrotreating reactor. They considered the hydrodesulphurization, hydrodenitrogenation and hydrodearomatization reactions and axial changes in concentration, partial pressure and temperature profiles were obtained with time. Chen and Ring[15] considered a pseudo homogeneous two dimensional reactor model of a fixed-bed hydrotreater and studied concentration and temperature profiles. Their model considered the heat conduction in the thermowell to predict the temperature difference between the thermowell and the catalytic bed. They concluded that if this difference is too high and ignored, could cause errors in the interpretation of pilot plant data. Mederos and Ancheyta [2] developed a dynamic heterogeneous one-dimensional model to predict the behavior of trickle-bed hydrotreating reactor with co-current and counter-current operation. They concluded that counter-current mode can have great potential to be used for deep hydrodesulfurization of oil fractions since it minimizes the inhibiting effect of some products in reactor zones where these species tend to concentrate in concurrent operation.

This paper reports experimental work and simulation results on the steady-state and dynamic behavior of a fixed-bed pilot-plant HDS reactor.

II. EXPERIMENTAL SECTION

The experiments were done in an isothermal pilot-plant reactor. The schematic diagram of the pilot plant setup is shown in fig. 1.

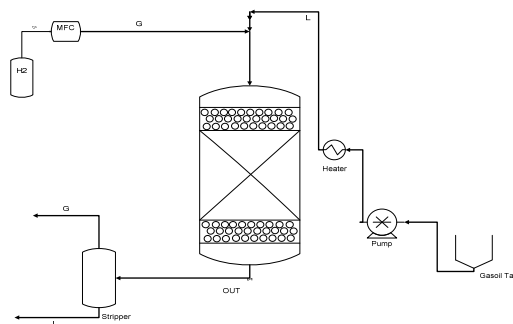


Fig 1. Schematic diagram of the pilot plant setup

The unit has been operated at temperature range of 340-380 °C and pressure range of 48-60 bar. Feed volumetric flow rate was 60-260 $\frac{cm^3}{h}$. The reactor length and internal diameter were 200 and 1.9 cm respectively and the catalytic bed length was 35 cm which was filled with CoMo/ Al_2O_3 catalyst. Above and below catalyst bed were packed with glass beads to provide a uniform gas and liquid flow. Hydrodesulfurization unit needs two different kinds of feeds. One for activation that consists of Dimethyl disulfide, hydrogen sulfide and carbon disulfide and other is used for separation of sulfur.

III. MATHEMATICAL MODEL

The reactor which has been used in pilot plant was operated isothermally. In this research we considered a pseudo-homogeneous two-dimensional model with axial convective and radial dispersion of mass. The dynamic mass balance equation in the catalyst bed is

$$\varepsilon_1 \frac{\partial C_i^l}{\partial t} = -U_1 \frac{\partial C_i^l}{\partial z} + \varepsilon_1 D_a^l \frac{\partial^2 C_i^l}{\partial z^2} + \varepsilon_1 D_r^l \left(\frac{\partial^2 C_i^l}{\partial r^2} + \frac{1}{r} \frac{\partial C_i^l}{\partial r} \right) - \rho_B \eta_j^l r_j^l \quad (1)$$

Where $i=S, N, A$

For catalyst pellets:

$$\frac{D_{el}^l}{r_p^2} \frac{\partial}{\partial r_p} \left(r_p^2 \frac{\partial C_{f,i}^s}{\partial r_p} \right) + r_j^l \rho_s \quad (2)$$

Where $i=S, H_2S, H_2$

Using Eq. 2, the effectiveness factor can be calculated with the following equation:

$$\eta_j^l = \frac{3 \int_0^{R_p} r_j^l (C_{S,T_S}) r_p^2 dr_p}{r_j^l (C_{S,li}^s, T_S^s)} \quad (3)$$

It was assumed that all holes of catalyst pellet were filled with liquid.

A. Model initial and boundary conditions and solution

For steady state and dynamic modeling it is necessary to define initial and boundary conditions. The initial and boundary conditions for liquid and solid phases are summarized in tables 1 and 2 respectively.

TABLE 1 INITIAL CONDITIONS

Condition	Liquid phase	Solid phase
$z=0$ $0 \leq r \leq R$	$C_i^l = (C_i^l)_0$	
$0 < z < L_B$ $0 \leq r \leq R$		
$z=L_B$ $0 \leq r \leq R$		

TABLE 2 BOUNDARY CONDITIONS

condition	Liquid phase	Solid phase
$z=0$ $0 \leq r \leq R$		
$z=L_B$ $0 \leq r \leq R$		-
$r=0$ $0 < z < L_B$		-
$r=R$ $0 < z < L_B$		-

The numerical method chosen to solve the developed partial differential equations is orthogonal collocation method,

a type of weight residual method (WRM) for elliptic PDE with two spatial domains. The orthogonal collocation is applied on both domains to yield a set of algebraic equations [16-18].

IV. RESULTS

A. Kinetics Evaluation

The following power law rate equations were considered for sulfur conversion although other expressions are available:

$$r_{HDS} = k C_S^n \quad (4)$$

$$k = k_0 \exp \left(\frac{-E}{RT} \right) \quad (5)$$

In which three kinetics parameters (k_0 , E , n) were unknown and to calculate them two basic assumptions were considered:

1. Isothermal reactor
2. Plug flow regime

Equation 4 can be written as:

$$\frac{1}{n-1} \left(\frac{1}{C_p^{n-1}} - \frac{1}{C_f^{n-1}} \right) = \frac{k}{LHSV} \quad (6)$$

Where C_f and C_p are sulfur concentration at reactor inlet and outlet respectively.

Kinetics parameters were obtained using Eq. 6 and fitting experimental data where the following kinetics equation was obtained with linear regression of 98.7 percent:

$$r_{HDS} = 64402.1 \exp \left(\frac{-92.66}{RT} \right) C_S^{1.4} \quad (7)$$

B. Steady State Results

The reactor governing equations have to be solved simultaneously to obtain sulfur axial concentration profile. Fig. 2 shows how sulfur concentration decreases in the liquid phase through the reactor.

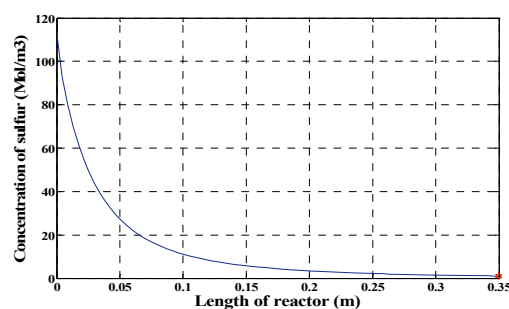
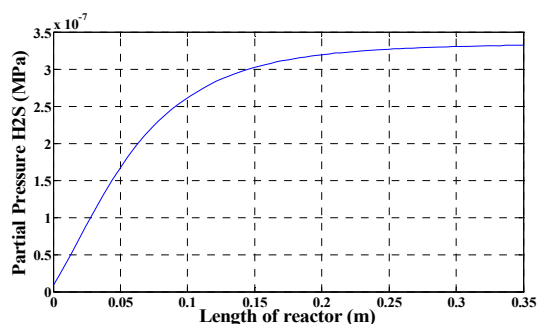
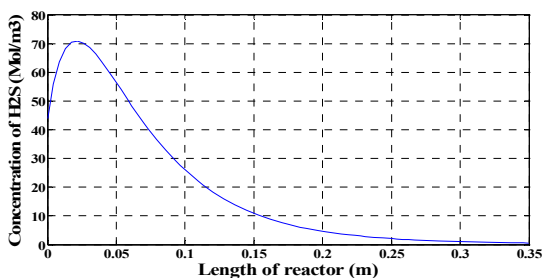


Fig 2. Sulfur axial concentration profile in liquid phase (feed rate: 140 cc/hr , P=50 bars inlet temperature=632.15 K)

The results reveal that there exists good agreement with experimental data and the sulfur concentration error in the reactor outlet was 3.8 percent compared to the experimental data and conversion was 99 percent. The partial pressure of H_2S in gas phase increases smoothly along the reactor bed as shown in Fig 3. But the H_2S concentration at the liquid phase increases and then decreases (Fig. 4). This phenomenon can be interpreted by mass transfer resistances. When the H_2S concentration in the liquid phase increases, the driving force of mass transfer from liquid to gas phase increases accordingly. This decreases the H_2S concentration in liquid phase.

Fig 3. Partial pressure of H₂S in gas phaseFig 4. H₂S concentration profile in liquid phase

Radial sulfur concentration profiles were obtained at various axial sections of the reactor (Fig.5). Note that the radial variation of sulfur concentration decrease when approach the end of reactor.

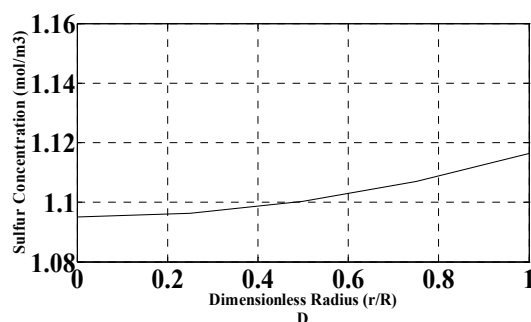
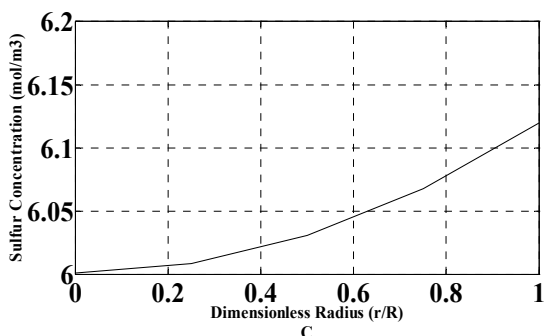
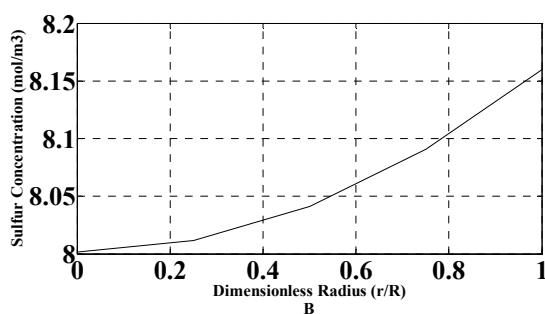
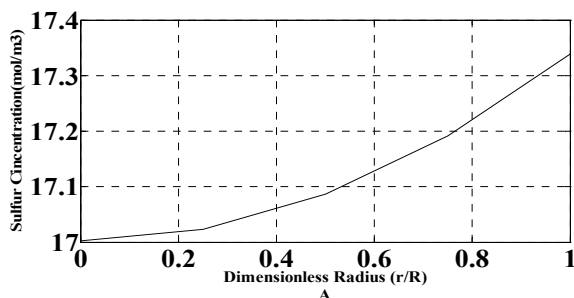
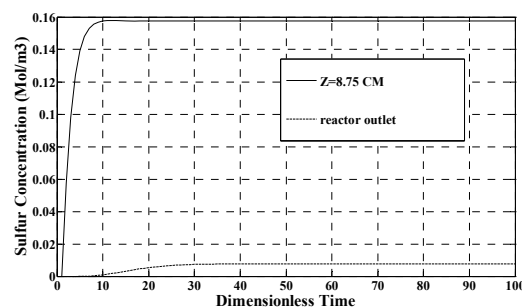


Fig 5. Sulfur radial concentration profile in liquid phase at various bed sections (feed rate: 140 cc/hr, P=50 bars, inlet temperature=632.15 K, A=0.25 Z, B=0.5 Z, C=0.75 Z, D=Z)

C. Dynamic Simulation

Figure 6 shows the variation of sulfur concentration at initial part of the catalytic bed (8.75 cm) and also at the reactor outlet with time. It was observed that the transition time was higher in the reactor outlet and estimated to be 11667 seconds

Fig 6. Sulfur concentration at 8.75 cm and the reactor outlet as a function of time (Feed rate: 140 cc/hr, P=50 bars inlet temperature=632.15 K, Dimensionless time is $\frac{U_L t}{L \epsilon_1}$, $\epsilon_1 = 0.08$)

V. CONCLUSIONS

A mathematical reactor model has been developed to numerically simulate the steady-state and dynamic behavior of a pilot-plant hydrotreater. The pilot plant reactor has been operated isothermally. Simulation results revealed suitable agreement with the pilot-plant experimental data. Simulation results indicated that the axial sulfur concentration decreases in the liquid phase while the hydrogen sulfide partial pressure increases smoothly in the gas phase. Hydrogen sulfide concentration in the liquid phase increases first and then decreases. The reason of this behavior can be interpreted by mass transfer driving force from liquid to gas phase which increases when the H₂S Concentration in liquid phase increases. Two dimension modeling result indicated that there is not much radial concentration variation and one dimensional approach can be considered. Dynamic simulation results proved that the transition time to steady state increases when reach to the reactor outlet.

Nomenclature

= Molar concentration of component i in the liquid phase,

$$C_i^L \left(\frac{\text{Mol}}{\text{m}^3} \right)$$

$C_{i,t}^s$ = Molar concentration of component i inside the solid filled with liquid phase, $\left(\frac{\text{Mol}}{\text{m}^3} \right)$

d_p = Catalyst particle diameter, m

$D_{e,i}^L$ = Effective diffusivity of component i inside a porous catalyst, ($\frac{m^2}{s}$)

D_a^L = Mass axial dispersion coefficient of liquid phase, ($\frac{m^2}{s}$)

D_r^L = Mass radial dispersion coefficient of liquid phase, ($\frac{m^2}{s}$)

K_{app} = Apparent reaction rate constant

LHSV= Liquid hourly space velocity, (hr^{-1})

n = Reaction Order

P = Reactor Pressure, (MPa)

r = Radial reactor coordinate, (m)

r_p = Radius of particle, (m)

r_j^L =Rate of reaction j per unit of catalyst mass in the liquid phase, $\frac{Mol}{Kg_s.S}$

t = Time, s

t' = Dimensionless Time

z = Axial reactor coordinate, m

Greek Letters

ϵ_B = Catalyst bed void fraction or catalyst bed porosity

ϵ_s = Catalyst particle porosity

ρ_B = Catalyst bulk (or bed) density, $\frac{Kg}{m^3}$

ρ_f = Density at process conditions of f phase, $\frac{Kg}{m^3}$

η_j^L = Catalyst effectiveness factor of reaction j in the liquid phase

Subscripts

A_{pp} = Apparent

B = Referred to reactor catalytic bed

f = Phase (gas, liquid or solid)

H_2 = Molecular hydrogen

H_2S = Hydrogen sulfide

L = Liquid phase

S = solid phase, inside catalyst pellet

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